

# PATENT SPECIFICATION

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## (54) IMPROVEMENTS RELATING TO THE PRODUCTION OF REDUCING GASES

(71) We, THE BRITISH PETROLEUM COMPANY LIMITED, of Britannic House, Moor lane, London E.C.2Y 9BU a British company, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the production of reducing gases the active components of which consist essentially of hydrogen and carbon monoxide.

The production of gases containing hydrogen and carbon monoxide is a well established industry. The main processes using hydrocarbon feedstocks are catalytic steam reforming and partial oxidation. The former, as the name suggests, reacts the hydrocarbons with steam and the product contains excess steam as well as carbon dioxide. Partial oxidation, which is usually a non-catalytic process, reacts the hydrocarbons mainly with oxygen. Although the product usually contains less steam and carbon dioxide, some is normally present and in addition it contains fine particles of carbon. For some purposes steam, carbon dioxide and carbon can be tolerated, but for other purposes, discussed in more detail hereafter, their presence is a severe disadvantage.

Catalytic partial oxidation processes have been proposed for the production of gases consisting essentially of hydrogen and carbon monoxide. However catalytic partial oxidation processes so far operated to produce such gases have been small, inefficient and expensive, since it has been the practice to supply the endothermic heat requirement externally to the metal catalyst tubes which are barely suitable at the temperature required.

In US Patent No. 2,039,603 it has been proposed that heat should be supplied by preheating the air to 800—1000°C. This solution, however, produces problems in its turn because pre-mixing of the hydrocarbon feedstock with this preheated air may lead to

decomposition of the hydrocarbon and deposition of carbon US Patent No. 2,039,603, therefore, requires that the air-hydrogen mixture is passed from the point of mixing into initial contact with the catalytic mass at a velocity at least sufficient to prevent flame, and then reducing the velocity as it flows in contact with the catalytic mass.

The present invention is based on further studies on the necessary conditions for successful operation when the heat is supplied by preheating the air.

According to the present invention therefore a process for the catalytic partial oxidation of hydrocarbons which comprises contacting a light hydrocarbon fraction with an oxygen-containing gas in the presence of a reforming catalyst under conditions of temperature and hydrocarbon:oxygen mole ratio such that the active components of the product gas consist essentially of hydrogen and carbon monoxide, as hereinafter defined, and in which the heat to the reaction is supplied entirely by heating the reactants and predominantly by pre-heating the oxygen-containing gas, is characterised in that the time between the contacting of the reactants and their entry into the catalyst bed is from 5 to 30 milliseconds and that mixing of the reactants is effected within that time, preferably by giving them a component of velocity at right angles to the direction of flow through the catalyst bed.

The term light hydrocarbon fraction means a fraction containing from C<sub>1</sub> to C<sub>4</sub> hydrocarbons and the hydrocarbons are preferably saturated hydrocarbons.

The lower the number of carbon atoms in the hydrocarbon the less is the risk of decomposition and carbon formation and the preferred feedstock contains one or more C<sub>1</sub> to C<sub>4</sub> hydrocarbons. Feedstocks may thus be light petroleum fractions, natural gas or other hydrocarbon-containing gases e.g. high flame speed gases such as coke oven gas.

Existing processes usually produce gases containing at least 6% volume of steam and

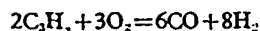
carbon dioxide and the term "consisting essentially of hydrogen and carbon monoxide" means a gas containing more than 94% volume of these gases, preferably at least 97%. Where, as is preferred, the oxygen-containing gas is not pure oxygen but is air, the product gas will contain an appreciable amount of nitrogen. Since nitrogen is an inert gas for the present purposes, the above definition excludes nitrogen and is based on the active components only.

In addition to the regulation of the contact time, it is also important to ensure good mixing of the reactants within the time allowed. Most preferably the reactants are given in horizontal component of velocity by injecting them tangentially into an inlet chamber. The injection may be through one or more ports in the chamber, and both reactants are preferably injected through the same port, e.g. by having a nozzle for the hydrogen projecting into the pipe for supplying the oxygen-containing gas, preferably at the point of entry of the pipe into the chamber.

The inlet chamber is preferably of the same diameter as the catalyst bed.

A part of the heat may be supplied by pre-heating the hydrocarbon feedstock but the amount that can be supplied in this way is limited by the risk of cracking the hydrocarbons. Preferably pre-heating of the hydrocarbons is limited to temperatures of 400°C maximum.

Conversion of the hydrocarbon substantially only to hydrogen and carbon monoxide, for example according to the equation,



is possible provided the temperature is sufficiently high and the hydrocarbon:oxygen ratio is kept near to the molecular ratios shown. The available oxygen content of any oxidising gases present in the feedstock would be included in the oxygen available for the reaction, e.g. half of the oxygen content of carbon dioxide would be considered available. Preferably the outlet temperature is in the range 800 to 1200°C more particularly in the range 900 to 1100°C. Too low a temperature tends to promote  $CO_2$ ,  $H_2O$  and  $CH_4$  formation; too high a temperature is uneconomic. Similarly too low a hydrocarbon:oxygen ratio produces  $CO_2$  and  $H_2O$  while too high a ratio will be wasteful. The reaction may be monitored by either a  $CO_2$ ,  $H_2O$  or  $CH_4$  analyser in the product stream and the temperature and/or quantity of oxygen fed adjusted as necessary. Since the heat to the reactants is supplied predominantly by pre-heating the oxygen containing gas, only this stream needs to be controlled to ensure that substantially only hydrogen and carbon monoxide are produced.

The oxygen containing gas is preferably air, this being less expensive than oxygen alone. The preferred pressures are in the range 1 to 7 bars absolute and the preferred linear velocity of the oxygen-containing gas in the inlet pipe is 300 to 800 ft/sec.

Any known type of hydrocarbon reforming catalyst may be used, provided it is capable of withstanding the operating conditions used. Such catalysts commonly comprise an iron group metal, particularly nickel, on a refractory support also possibly containing one or more known promoters, e.g. alkali metals, alkaline earth metals, or uranium whose main object is to suppress carbon formation. Thus the support may be, for example  $\alpha$ -alumina, silica, an alumino-silicate, magnesia, or a proprietary support currently used in steam reforming.

The preferred catalyst formulation range is as follows:—

Nickel	3—15 % wt.	85
Uranium	0—10 % wt.	
Barium	0—1.7 % wt.	
Potassium	0—0.5 % wt.	

Tolerance of iron group metal catalysts to sulphur increases with temperature and will be greater than at, for example, the conventional steam reforming temperatures of 800°C or less. Preferably, however, the feedstocks are low in sulphur compounds, for example, less than 30 ppm by weight of sulphur.

The reaction is exothermic, releasing in the case of propane in the equation above, approximately 51 kilocalories/mole of propane at 25°C so that the reactants pre-heat temperature will be less than the reaction temperature. With no external heating the reactor can have a refractory lining and operate adiabatically and the amount of pre-heat required can readily be determined by experiment or calculation. Preferably the oxygen-containing gas is pre-heated to a temperature within the range 700 to 1100°C, particularly 800 to 1000°C.

In the case of a preferred fixed-bed reactor, this may operate with down, radial, or up-flow. Since the preferred catalysts given above are regenerable, fixed beds of catalyst can be operated on a swing-reactor system with two or more beds in parallel, one or more of the beds being regenerated if this becomes necessary while the other or others are on stream and vice versa. Any carbon formed which may be deposited on the catalyst can thus be burnt off with an oxygen containing gas in the absence of the hydrocarbon feedstock. Alternatively a fluidized bed of catalyst can be used with or without recycle between the reactor and regenerator.

The size of the catalyst particles will depend on whether a fixed or fluidized bed is used being preferably 15 to 30 mm diameter

for fixed beds and 0.2 to 2.0 mm diameter for fluidized beds. Space velocities may be in the range 5000 to 15000 stp volumes of product gas per hour per volume of catalyst. As indicated above the hydrocarbon and oxygen-containing gas are preferably fed in at approximately the stoichiometric quantities for conversion only to hydrogen and carbon monoxide. The space velocities of the reactants can thus be readily calculated as indicated above for any given feedstock and oxygen-containing gas.

The product gas may be used for any known purpose, but it is particularly suitable for the reduction of ores, particularly iron ore, either in the upper part of a blast furnace or in a specialised iron ore reduction plant e.g. one operating with a fluidized bed of iron ore particles. Such reduction processes require temperatures of 550°C or higher and at such temperatures carbon dioxide and steam act as oxidising gases. Even small amounts of these gases will thus nullify to an undesirable extent the reducing power of the hydrogen and carbon monoxide. Particles of carbon in the gas are also undesirable since these will not be converted to oxides of carbon under the reducing conditions. With existing processes and qualities of gas it is, of course, possible to remove the carbon dioxide, steam, and carbon by cooling and washing but this is obviously uneconomical, particularly so where the gas is to be used at high temperature.

The present invention therefore includes a process for the reduction of ores, particularly iron ore, comprising contacting a light hydrocarbon fraction with an oxygen-containing gas in the presence of reforming catalyst as previously described and thereafter passing said gas without substantial cooling or removal of contaminants to the ore reduction step.

The invention is illustrated with reference to the accompanying drawing which is a flow diagram of a catalytic partial oxidation unit operated according to the present invention.

In the drawing, a hydrocarbon feedstock storage tank 1 has an outlet pipe 19. In this line are filter 20, and pump 2 and connected with it are a pump pressure control system 3 and static pressure relief system 4. A pressure gauge is shown at 5 and a hydrocarbon flow control valve and monitor at 6. The hydrocarbon flows through line 19 through valve 18a to an upflow fixed bed reformer 9 having an inlet chamber 8. The reformer will be described in more detail hereafter.

Air is drawn in through line 21 and compressor 11. A portion of this air may flow as cold air and through line 22 and control valve 17 to the reformer 9. Another portion is preheated by passing through valve 23 into heater 12. This may be a pebble heater or Cowper stove heated by supplying fuel through line 15 and air through line 14 to

a burner (not shown). The waste gases are vented through line 13. A second heater 12a indicated by the dotted lines would be used in parallel to ensure a continuous supply of hot air. Hot air flows through line 16 to mix with cold air in the required proportions for the temperature required and enters the reformer 9 via valve 18b which is linked with the hydrocarbon inlet valve 18a. A third linked valve 18c is used to supply nitrogen from line 7 to purge the reformer 9.

In the event of a planned or unplanned closure of the feedstock valve, the nitrogen purge would remove the feedstock downstream of the feedstock valve 18a in order to prevent thermal cracking which may produce deposits in the reformer 9.

Inlet chamber 8 is a swirl chamber having a tangential inlet for the hot air and a hydrocarbon injection nozzle projecting into it at the point of entry into the chamber. The nozzle has a spray angle of 45°.

The reforming catalyst is supported by a grid (not shown) and product gas is withdrawn through line 18.

In a specific example propane was used as the hydrocarbon feedstock in the plant described above under the following conditions.

#### Catalyst Bed:

1ft dia×5ft depth

#### Swirl chamber:

1ft dia×2½ inches depth

#### Inlet to chamber:

1½ inches diameter

#### Catalyst:

5% nickel and 2% uranium oxide on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

#### Reactants:

180 lbs/hour propane, nil preheat

8 lbs/hour steam at 912°C

10,800 ft<sup>3</sup> stop air/hour at 912°C

9 milliseconds time between initial contacting and entering catalyst bed

#### Product Gas:

18900 ft<sup>3</sup> stp/hour

4700 ft<sup>3</sup> stp/ft<sup>3</sup> catalyst/hour

890°C

4 p.s.i.g.

#### Product Gas Analysis

Hydrogen

Carbon monoxide

Nitrogen

Methane

Steam

Carbon dioxide

Non-gaseous products

mol %

54.6

44.6

0.1

0.6

0.1

Trace

#### Product Gas Yield:

89.7 Therms/100 therms process feed.

#### WHAT WE CLAIM IS:—

1. A process for the catalytic partial oxidation of hydrocarbons comprising contacting a

- light hydrocarbon fraction with an oxygen-containing gas in the presence of a reforming catalyst under conditions of temperature and hydrocarbon:oxygen mole ratio such that the active components of the product gas consist essentially of hydrogen and carbon monoxide, as hereinbefore defined, and supplying the heat to the reaction entirely by heating the reactants and predominantly by heating the oxygen-containing gas, characterised in that the time between the contacting of the reactants and their entry into the catalyst bed is from 5 to 30 milliseconds and that mixing of the reactants is effected within that time, preferably by giving them a component of velocity at right angles to the direction of flow through the catalyst bed.
2. A process as claimed in claim 1 wherein the light hydrocarbon fraction consists of  $C_1$ — $C_4$  saturated hydrocarbons.
3. A process as claimed in claim 1 or 2 wherein the product gas contains at least 97% volume of hydrogen and carbon monoxide.
4. A process as claimed in any of claims 1 to 3 wherein the reactants are mixed by injecting them tangentially into an inlet chamber.
5. A process as claimed in claim 4 wherein the reactants are injected through a port in the chamber, both reactants being injected through the same port.
6. A process as claimed in claim 4 or 5 wherein the inlet chamber is the same diameter as the catalyst bed.
7. A process as claimed in any of claims 1 to 6 wherein the catalytic partial oxidation outlet temperature is within the range 800 to 1200°C, preferably 900 to 1100°C.
8. A process as claimed in any of claims 1 to 7 wherein the catalytic partial oxidation pressure is 1 to 7 bars absolute.
9. A process as claimed in any of claims 1 to 8 wherein the reforming catalyst comprises from 3 to 15% wt of an iron group metal, particularly nickel, on a refractory support.
10. A process as claimed in any of claims 1 to 9 wherein the oxygen-containing gas is preheated to a temperature within the range 700 to 1100°C, preferably 800 to 1000°C.
11. A process as claimed in any of claims 1 to 10 wherein the hydrocarbon feedstock is not preheated or is preheated to a temperature of not more than 400°C.
12. A process as claimed in any of claims 1 to 11 wherein the product gas space velocity is 5000 to 15000 stp volumes/volume of catalyst/hour.
13. A process for the reduction of ores, particularly iron ore, comprising forming a product gas consisting essentially of carbon monoxide and hydrogen by a process as claimed in any of claims 1 to 12 and passing said gas without substantial cooling or removal of contaminants to an ore reduction process.
14. A process as claimed in claim 1 substantially as described with reference to the drawing.
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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

